

学校编码：10384

分类号_____密级 _____

学 号：200125057

UDC_____

厦 门 大 学
硕 士 学 位 论 文

微波陶瓷表面化学镀铜工艺及机理研究

Technical and Mechanistic Investigation for Electroless
Copper Plating on Microwave Ceramic Substrates

谷 新

指导教师姓名： 林 昌 健 教 授

专 业 名 称： 物 理 化 学

论文提交日期： 2004 年 6 月

论文答辩日期： 2004 年 6 月

学位授予日期： 2004 年 月

答辩委员会主席：_____

评 阅 人：_____

2004 年 6 月

厦门大学博硕士论文摘要库

目 录

中文摘要	1
英文摘要	1
第一章 绪 论	1
1.1 化学镀铜概述	1
1.2 化学镀铜基本原理	2
1.2.1 化学镀铜的热力学条件	2
1.2.2 化学镀铜的动力学条件	3
1.2.3 化学镀铜的反应机理	4
1.2.4 化学镀铜反应的电化学研究	7
1.3 陶瓷表面化学镀铜	9
1.3.1 微波陶瓷简介	9
1.3.2 陶瓷表面化学镀前处理	10
1.3.3 化学镀铜溶液	18
1.4 本文研究目的和主要内容	20
参考文献	21
第二章 实 验	29
2.1 实验装置及工艺条件	29
2.1.1 试剂	29
2.1.2 实验装置	29
2.1.3 实验过程	30
2.2 实验方法	31
2.2.1 pH 值的测定	31
2.2.2 沉积速率的测定	31
2.2.3 镀液稳定性的评价	32
2.2.4 镀层电阻率的测定	32
2.2.5 镀层形貌的扫描电子显微镜(SEM)表征	33

2.2.6 镀层结构的表征	34
2.2.7 镀层与基体结合力的测量	34
2.2.8 电化学测试	35
参考文献	36
第三章 陶瓷表面化学镀铜工艺研究	38
3.1 前言	38
3.2 工艺条件对镀铜速度和镀液稳定性影响的研究	39
3.2.1 温度对镀速和镀液稳定性的影响	39
3.2.2 pH 值对镀速和镀液稳定性的影响	41
3.2.3 甲醛浓度对镀速和镀液稳定性的影响	42
3.2.4 2,2'-联吡啶对镀速和镀液稳定性的影响	43
3.2.5 三乙醇胺对镀速和镀液稳定性的影响	44
3.2.6 $[\text{Cu}^{2+}]/[\text{EDTA}]$ 的比值对镀速的影响	45
3.3 陶瓷基铜镀层结合力和电阻率的测量	46
3.3.1 粗化时间对镀层结合强度的影响	46
3.3.2 电阻率的测量结果	47
3.4 镀层形貌和结构的表征结果	48
3.4.1 镀层形貌的 SEM 照片	48
3.4.2 镀层晶体结构的 XRD 谱图	49
3.5 添加剂对化学镀铜影响的研究	50
3.5.1 添加剂 2,2'-联吡啶对镀层形貌的影响	50
3.5.2 添加剂 V_2O_5 或 NH_4VO_3 对化学镀铜速度和镀层形貌的影响	51
3.5.3 添加剂 CeCl_3 对化学镀铜速度、镀液稳定性和镀层形貌的影响	53
3.6 结论	56
参考文献	56
第四章 化学镀铜机理的电化学研究	59
4.1 络合剂和添加剂对化学镀铜影响的电化学研究	59
4.1.1 引言	59
4.1.2 添加剂 2,2'-联吡啶的影响	60

4.1.3 主络合剂(EDTA)的影响.....	61
4.1.4 辅助络合剂(TEA)的影响.....	63
4.2 化学镀铜过程混合电位本质的研究.....	65
4.2.1 引 言.....	65
4.2.2 钯活化的铜表面和化学镀铜过程混合电位的测定.....	66
4.2.3 新生铜表面化学镀铜过程混合电位的测定.....	68
4.2.4 基体活化工艺对混合电位-时间曲线的影响.....	72
4.3 结 论.....	73
参考文献.....	74
作者在攻读硕士学位期间发表与交流的论文.....	77
致谢.....	78

Table of Contents

Abstract in Chinese	
Abstract in English	
Introduction	1
1.1 General	1
1.2 Fundamental of electroless copper plating	2
1.2.1 Thermodynamics of electroless copper plating.....	2
1.2.2 Kinetics of electroless copper plating.....	3
1.2.3 Mechanism of electroless copper plating.....	4
1.2.4 Electrochemical study of electroless copper solution.....	7
1.3 Electroless copper plating on ceramics	9
1.3.1 General of microwave ceramics.....	9
1.3.2 Pretreatment of electroless copper on ceramics.....	10
1.3.3 Solution of electroless copper plating.....	18
1.4 Objectives and contents of this dissertation	20
References	21
Experimental	29
2.1 Instruments and procedure	29
2.1.1 Reagents.....	29
2.1.2 Instruments.....	29
2.1.3 Procedure.....	30
2.2 Methods of Experiment	31
2.2.1 Tests of pH value of the solution.....	31
2.2.2 Tests of the plating rate.....	31
2.2.3 Estimates of the stability of the electroless copper solution.....	32
2.2.4 Characterization of the resistivity of copper coatings.....	32
2.2.5 SEM characterization of the copper coatings.....	33

2.2.6 XRD characterizations of coatings crystal structure·····	34
2.2.7 Tests of the bond stress·····	34
2.2.8 Electrochemistry tests of the electroless copper solution·····	35
References ·····	36

Investigation of Electroless Copper Plating Techniques ·····38

3.1 Introduction·····38

3.2 Study of Electroless Copper Plating on microwave ceramics·····39

3.2.1 Effect of temperature on the plating rate and stability of electroless copper solution·····	39
3.2.2 Effect of pH value on the plating rate and stability of electroless copper solution·····	41
3.2.3 Effect of the concentration of HCHO on the plating rate and stability of electroless copper solution·····	42
3.2.4 Effect of the concentration of 2,2'-dipyridine on the plating rate and stability of electroless copper solution·····	43
3.2.5 Effect of the concentration of TEA on the plating rate and stability of electroless copper solution·····	44
3.2.6 Effect of the value of $[Cu^{2+}]/[EDTA]$ on the plating rate and stability of electroless copper solution·····	45

3.3 Tests of bonding stress and resistivity of the electroless copper coatings·····46

3.3.1 Effect of the time of chemical roughen on the the bond stress·····	46
3.3.2 Results of the resistivity of the electroless copper coatings·····	47

3.4 morphologies and crystal structure of the electroless copper coatings·····48

3.4.1 SEM photos of the coatings·····	48
3.4.2 XRD patterns of the electroless copper·····	49

3.5 Effects of additives on the electroless copper plating·····50

3.5.1 Effect of 2,2'-dipyridine on the surface morphologies of the coatings·····	50
3.5.2 Effects of the of V_2O_5 or NH_4VO_3 on the plating rate and surface	

morphologies of the coatings.....	51
3.5.3 Effects of the of CeCl_3 on the plating rate , stability of the solution and surface morphologiesof the coatings.....	53
3.6 Conclusions.....	56
References.....	56
 Electrochemical study of the mechanism of electroless copper plating.....	 59
4.1 Electrochemical study of the effects of the chelating agents or additives.....	59
4.1.1 Introduction.....	59
4.1.2 Effect of the concentration of 2,2 -dipyridine.....	60
4.1.3 Effect of the concentration of Na_2EDTA	61
4.1.4 Effect of the concentration of TEA.....	63
4.2 In situ investigation on the Behaviors of Mixed Potential in Electroless copper plating.....	65
4.2.1 Introduction.....	65
4.2.2 Mixed potential-time curve of-electroless copper plating on Pd-activated copper substrates or on Pd-activated ceramic substrates.....	66
4.2.3 Mixed potential-time curve of electroless copper plating on fresh coppersubstrates.....	68
4.2.4 Effects of the activation process of substrates on the mixed potential-time curve.....	72
4.3 Conclusions.....	73
References.....	74
 Publications list during master study.....	 77
 Acknowledgements.....	 78

微波陶瓷表面化学镀铜工艺及机理研究

摘 要

化学镀不需要外加电源，可以在导体和非导体上进行，具有良好的均镀能力。其核心技术还是镀液的组成和性能，经过 50 多年的应用和发展，已经取得了长足的进展，但镀液的稳定性和沉积速度仍然是一对未能较好解决的矛盾。纵观大量相关的研究，结合微波陶瓷器件的物理性能要求和微波陶瓷自身的特点，本文进行了如下几方面的研究和探讨：

1. 综述了非金属表面化学镀前处理工艺的现状和发展，对陶瓷化学镀的粗化和活化工艺的新进展进行了评述，侧重讨论了几种活化工艺的特点和进展，并展望了今后的发展方向。

2. 在大量的实验基础上，成功地优化了一种沉积速度快、镀液稳定性好的化学镀铜的最佳工艺条件。镀液的主要组成包括 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 15g/L， $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ 28g/L，三乙醇胺（78%）15mL/L，2,2-联吡啶 10ppm，甲醛（37%）20mL/L 及聚乙二醇（MW600）80ppm。可在陶瓷表面获得表面光亮均一，具有较低电阻率和良好结合力的铜镀层。

研究了 2,2-联吡啶、 Ce^{3+} 、 V_2O_5 和 NH_4VO_3 作为添加剂对镀速和镀层形貌的影响，还研究了 Ce^{3+} 对镀液稳定性的影响。较低浓度的 2,2-联吡啶， Ce^{3+} 和 NH_4VO_3 均能在一定程度上提高镀速，而较高浓度又将降低镀速；但是 V_2O_5 只能降低镀速。这几种添加剂均能在一定程度上使镀层晶粒细化，从而改善镀层的表面形貌。

3. 采用线性扫描伏安技术研究了化学镀铜液的极化性能。较低浓度的 2,2-联吡啶（5ppm）能提高甲醛的氧化峰电流、有利于甲醛的阳极氧化；而三乙醇胺能降低甲醛氧化峰电流、阻碍甲醛的阳极氧化。从阴极极化曲线

可检测到 Cu^{2+} 的 EDTA 络合物和 Cu^{2+} 的 TEA 络合物的还原峰, EDTA 和 TEA 可提高各自对应的铜的络合物的还原峰电流值而降低另一个络合物的还原峰电流值; 而 2,2'-联吡啶降低两个阴极还原峰的峰电流值。该结果与沉积速度的结果具有良好的一致性。

4. 现场测量了陶瓷基体、铜基体化学镀铜过程混合电位-时间曲线, 详细研究了化学镀的诱发过程。考察了络合剂和添加剂的浓度以及 pH 值对混合电位-时间曲线的影响, 结果表明随着溶液中络合剂或稳定剂浓度的增加, 混合电位-时间曲线负移, 诱发时间增加。高 pH 值能减少诱发时间, 而使混合电位-时间曲线正移。结合阴极阳极极化曲线以及双电层理论解释了各种影响因素。比较活化工艺对混合电位-时间曲线的影响, 发现较高的活化温度能大大减少诱发时间, 提高镀速, 而且还能大大减少活化时间。对新生铜表面化学镀铜过程混合电位时间曲线的研究发现, 其诱发过程是一个缓慢激活过程, 所对应的电位-时间曲线是一个略微倾斜的平台, 不同于钯活化的诱发过程, 由此也说明了贱金属活化工艺不及贵金属活化工艺的原因, 对化学镀铜的生产实践具有一定的指导意义。

关键词: 微波陶瓷; 化学镀铜; 电化学研究

Technical and Mechanistic Investigation for Electroless Copper Plating on Microwave Ceramic Substrates

Abstract

Electroless copper plating is a wide-used technique involving the deposition of metal from solution onto the surfaces without external electric voltage. And it can form a homogeneous metallic coatings on insulators or conductors. In the past more than fifty years, electroless copper technology has been studied and improved rapidly, and widely applied in many fields. Meanwhile, the plating solution composition is a key factor, and the solution stability and the plating rates are still a pair of contradictions in the technique. Based on the review of most literature in this field, and taking into account of the needs and the characteristics of microwave ceramic devices, we have focused the investigation of technique and mechanism for the electroless copper plating on ceramic substrates. The major results are outlined as follows:

1. The pretreatment processes for electroless plating of non-metallic materials, especially the chemical roughening and activating processes were reviewed. The technical characteristics of several activating processes were discussed, and the aim of the developing of pretreatment process was forecasted.

2. Based on the numerous experiments, we have successfully optimized a technique of electroless copper plating on ceramic substrate, which possesses faster plating rate and good solution stability. The plating aqueous solutions consisted of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (15g/L), $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (28g/L), Triethanol-amine (15ml/L), 2,2'-dipyridine (10ppm), HCHO (20ml/L) and surfactants. The operating condition was also optimized. The coatings deposited were uniform, bright and lower resistivity as well as strong bonding stress by this optimized technique.

The concentration of 2,2'-dipyridine, Ce^{3+} , V_2O_5 or NH_4VO_3 has a distinct

effect on the plating rate and the surface morphology of the coatings. Lower concentration of 2,2'-dipyridine, Ce^{3+} or NH_4VO_3 can increase the plating rate, while higher concentration of them will slow the plating rate. But V_2O_5 will decrease the plating rate. With the increasing of the Ce^{3+} , the solution will become unstable. And all of them can reduce the grain size and improve the surface morphology of the coatings deposited in a specific range of the concentration.

3. Linear sweep voltammetry was applied to analyse the polarization behavior for the copper deposition in various plating solutions. The addition of 2,2'-dipyridine increases the peak current of formaldehyde oxidation and is beneficial to formaldehyde oxidation in a specific range of concentration, while TEA decreases the peak current of formaldehyde oxidation. Two cathodic peaks due to copper () reduction of TEA chelating and copper () reduction of EDTA chelating were discovered. The EDTA increases the reduction peak current of Cu-EDTA and decreases that of Cu-TEA, While TEA increases the reduction peak current of Cu-TEA, and it decreases that of Cu-EDTA. 2,2'-dipyridine also decreases the reduction peak current of Cu-TEA and Cu-EDTA. The experiment results are consistent with the weight gain measurement.

4. The mixed potential as a function of time was measured during the electroless copper plating on ceramic and copper substrates, and the induction process was discovered successfully. The effects of the chelating agents, additives and pH value on the mixed potential-time curves were investigated. The results indicate that the mixed potential-time curves shift in negative direction and the induction time becomes longer with the increasing concentration of the chelating agents or the additives in the solution. Higher pH values in the solution can shorten the induction time and make the potential-time curves more negative. The

activation process can influence the induction time, higher activation temperature decreases the induction time greatly and increase the plating rate at the same time. It takes much longer induction time for plating copper on a fresh-copper-activated copper substrate than that on the Pd-activated copper substrate. On the basis of the results, we furthermore explained the reason why the non-noble-metal activation process is inferior to the noble-metal activation process in the electroless copper plating.

Keywords: **Microwave ceramic substrate, Electroless copper plating, Electrochemical study**

厦门大学博硕士论文摘要库

第一章 绪 论

1.1 化学镀铜概述

化学镀是一种应用广泛的表面处理技术。所谓化学镀就是指在不需要外加电源的条件下，具有自催化活性的金属离子在催化活性表面被还原剂还原出来、在基体表面形成一层金属或合金镀层的技术，所以又叫非电镀（electroless plating）或化学沉积(chemical deposition)。

化学镀有化学镀镍、铜、钴、银、金、钯、铂、合金镀、复合镀等。由于化学镀不需要外加电源、不受基体的限制、镀液具有良好的均镀能力及各种镀层具有优良的物理化学性能，已经广泛应用于航天、电子、食品、机械、汽车、石油化工以及新兴的纳米技术等领域^[1-8]。

1947，Narcus 首次报道了化学镀铜，但初始阶段的化学镀铜液的稳定性很差，镀液极易自动分解，且施镀范围不能控制，所有与镀液接触的部位都有沉积物^[9]，基本不具备工业应用的条件。直到二十世纪五十年代中期，随着印刷电路板（PCB）通孔金属化的发展，化学镀铜得到了最早的应用，为化学镀铜技术提供了巨大的市场，同时也促进了化学镀铜技术的发展^[3]；开发出了与今天化学镀铜类似的最早化学镀铜液为以甲醛为还原剂的碱性酒石酸铜镀液。化学镀铜技术在二十世纪六十年代取得了长足的进步，主要表现在：（1）开发成功胶体 Sn-Pd 商品技术^[10]；（2）络合剂除酒石酸盐之外，还采用了 EDTA、烷基醇胺等；（3）发现一系列有效的稳定剂，显著地改善了化学镀铜溶液的稳定性。化学镀铜技术在二十世纪七十年代开始走向成熟，镀液具有较高的稳定性，工业应用得到了突破性的进展，出现了镀液分析调整全自动控制的生产线。二十世纪八十年代高新技术的发展驱动着印刷电路产业技术的方向，市场要求印刷电路板高密度的发展，使得孔金属化成为印

刷电路制造的中心环节之一；为保证产品的可靠性，对化学镀铜层的性能，特别是延展性、抗张强度提出了十分苛刻的要求，这一时期的化学镀铜仍然采用经典工艺的形式；然而有关工艺材料和控制技术，从内容和水平两方面发生了重大的革新。目前，化学镀铜不仅在宽广的操作条件下长时间镀液保持稳定，而且化学镀过程状态可以预测，镀层性能优良^[11]。

化学镀铜的重要性仅次于化学镀镍，在电子工业中用途最广^[12]。用化学镀铜使活化的非导体表面导电后，制造通孔的双面或多层印刷电路板^[13]；化学镀铜层还由于其本身具有良好的导电性以及良好的抗电迁移能力而被广泛应用于电子元器件行业中^[14-18]，在电子元器件中的应用主要是电子陶瓷表面的金属化。化学镀铜层还可作为非导体电镀的金属化后电镀等；也可以用于雷达反射器、同轴电缆射频屏蔽、天线罩、底板屏蔽和热辐射。化学镀与电镀相比，通常说来，电镀的成本较化学镀低，而化学镀的主要优点集中在镀层性能方面^[19]：镀层厚度均匀，无明显的边缘效应，不受镀件形状限制；镀层晶粒细小、致密、孔隙少，呈光亮或半光亮，比电镀层更加耐腐蚀；无需电解设备及附件；能在非导体(塑料、玻璃、陶瓷等)上沉积；某些镀层具有特殊的化学、机械或者磁性能。

1.2 化学镀铜基本原理

1.2.1 化学镀铜的热力学条件

化学镀铜发生在水溶液与具有催化活性的固体界面，由还原剂甲醛将铜离子还原为金属铜，从反应结果来看，总反应是由两个半反应组成的氧化还原电池反应，每个电极反应和对应的电极电位为^[20]，



Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士论文摘要库